

MSc II - Sem III - Oct. 2016

Organic Chemistry - Paper I

QP Code : 77559

(2½ Hours)

[Total Marks : 60

- N.B. : (1) Answer all questions
(2) Figures to the right indicate full marks.

1. (a) Answer any two of the following :-

- (i) Explain in detail generation of carbocation from the following :-
(I) Heterolytic fission of neutral species
(II) Via addition of cation to neutral species
(ii) Discuss stereochemical evidence for neighbouring group participation reaction.
(iii) Explain hard and soft electrophiles and nucleophiles on the basis of FMO.
(iv) Draw molecular orbitals of buta-1,3-diene and indicate number of nodes and mirror symmetry.

(b) Answer any one of the following :-

- (i) Explain mechanism of a reaction involving ketene reactive intermediate.
(ii) What are pericyclic reactions? Give classification and elaborate on how FMO helps in understanding the same.

2. (a) Answer any two of the following :-

- (i) Explain cheletropic reactions of alkenes with singlet carbene and reaction of alkenes with SO_2 .
(ii) Define electrocyclic reaction. Comment giving suitable examples involving π and σ bond to yield cyclic product and vice-versa.
(iii) Using FMO approach explain sigmatropic rearrangement.
(iv) Give synthesis of citral using pericyclic process.

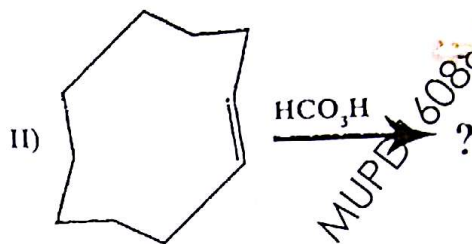
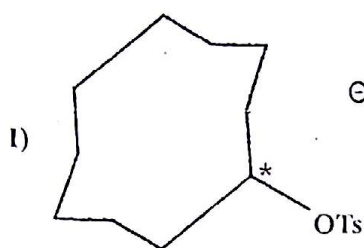
(b) Answer any one of the following :-

- (i) Draw the correlative diagram for $4\pi + 2\pi$ cycloaddition reaction.
(ii) Explain the mechanism of Claisen rearrangement.

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3. (a) Attempt any two of the following :-

- (i) Suggest the symmetry elements and point group present in naphthalene.
- (ii) Complete the following reactions and suggest the mechanism with stereochemical outcome.



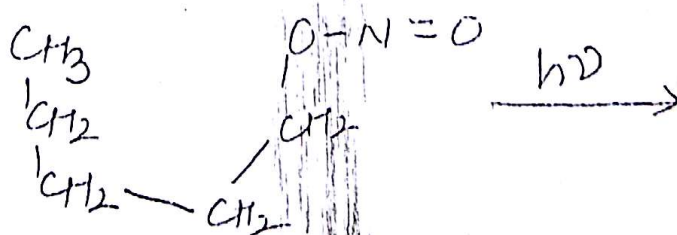
- (iii) Draw all the possible conformers of decalin.
'Cis-decalin though dissymmetric cannot be resolved.' Explain the statement.
- (iv) The products of deamination of α -aminocyclohexanol depend upon the conformation of substrate. Explain this observation with mechanism.

(b) Attempt any one of the following :-

- (i) Conformation reactivity correlation depends on selection of substrate. Explain this statement by considering conformationally rigid diastereomers.
- (ii) Explain the reactivity and mechanism of E₂ elimination as shown by pair of epimers of menthyl chloride.

4. (a) Attempt any two of the following :-

- (i) Complete the following reaction, give its name and mechanism:

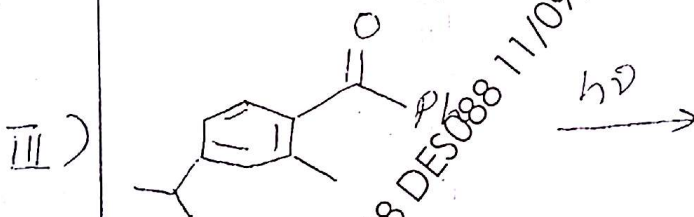
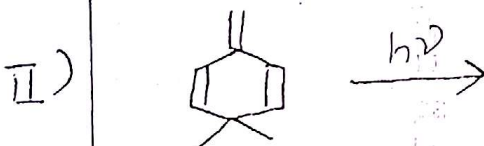
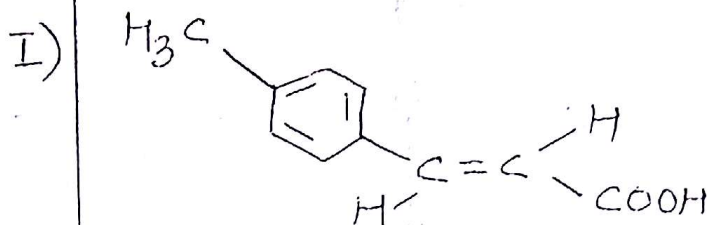


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(ii) Give two examples for each of the following reactions:

- (a) Singlet oxygen reaction
 (b) 1, 4 addition reaction of arenes.

(iii) Complete the following reactions:



Draw Jablonski diagram and explain various possible phenomena which occur during absorption of the light by the organic molecule.

Attempt any one of the following:-

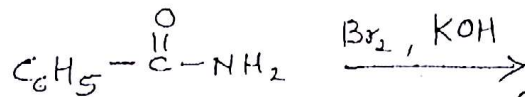
- (i) Explain the mechanism of aza di- π methane rearrangement reaction with a suitable example.

TURN OVER

- (ii) What are photochemical quenchers? Explain the principle of photochemical quenching and give two examples of photochemical quenchers.

5. Answer any four of the following :-

- (a) How are arynes synthesized from -
 (i) Anthranilic acid
 (ii) Aryl halide
 (iii) Phthaloyl peroxide ?
- (b) Briefly explain the mechanism of the following reaction and identify the reactive intermediates



- (c) Explain ene reaction and give its mechanism.
 (d) Give synthesis of vitamin -D from δ -dehydrocholesterol.
 (e) Cyclodecene on bromination gives 1,6- dibromocyclodecane. Explain.
 (f) Explain I-strain concept.
 (g) Give the mechanism of the vapour phase photolysis of cyclohexanone.
 (h) Complete the following reaction and give its mechanism.

